Dissertation

Removal of Polymer Coating with Supercritical Carbon Dioxide

Submitted by

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Abstract of Dissertation

Removal of Polymer Coatings with Supercritical Carbon Dioxide

This work investigates the use of supercritical fluids, and carbon dioxide in particular, for the removal of polymer coatings. Research into new supercritical fluid applications is nearly always based on a trial and error approach, and frequently requires evaluating each operation on a case-by-case basis. A significant improvement in this approach is accomplished with the development of a framework in which polymer-CO_2 interactions can be evaluated and the number of experimental trials reduced.

The basic model developed is built upon the three-component solubility parameter (HSP) concept, which is widely used in the coatings industry to aid in the selection of solvents. Temperature and pressure dependent HSP values have been develop for supercritical CO_2, using a methodology extendable to other supercritical fluids. Equations were also developed to calculate HSP's for cosolvents and polymers. With the solvent, cosolvent, and polymer thus fully characterized in terms of the HSP values, the systems are then analyzed in terms of the like and unlike (solvent/polymer, cosolvent/polymer, and solvent/cosolvent) binary pairs. In addition to this study, consideration of specific interactions, such as Lewis acid/base interactions between the solvent and polymer or between the cosolvent and polymer are examined for their role in determining a favorable (polymer coating removal) result.

The model was tested on two real-world applications: involving poly(methyl methacrylate) (PMMA) and polycarbonate (PC) coatings. Several organic liquids were evaluated as cosolvents, including at least one example of a non-polar fluid, a Lewis acid, and a Lewis base. Results of this study found the following interactions, listed in order of importance in the removal of polymer coatings, to be (1) specific interactions between the solvent and polymer, in the case of PMMA and CO_2, or specific interactions between the cosolvent and polymer, in the case of PC and CO_2, (2) weaken polymer/polymer interactions as a result of polymer swelling and subsequent lowering of the polymer HSP values, (3) specific interactions between the solvent and cosolvent are not necessary and in the case of specific interactions between the cosolvent and polymer, may be undesirable.

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……..“I hear and I forget, I see and I remember, I do and I understand.”

Confucius

To Jim Rubin, for taking the trip with me and making the journey worthwhile…..

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T	Temperature
T_c	Critical temperature
T_r	Reduced temperature, T/T_c
T_{br}	Reduced boiling temperature, T_b/T_c
T_g	Glass transition temperature
P	Pressure
P_c	Critical pressure
P_r	Reduced pressure, P/P_c
V	Volume
r	Density
r_r	Reduced density, ρ/ρ_c
α^p	Polarizability
m	Dipole moment
I	Ionization potential
s	Collision diameter
r	Distance between molecules
r_o	Equilibrium distance between molecules
Q	Quadrupole moment
U	Total energy of a system
${}_1Q_2$	Heat transferred to a system
${}_1W_2$	Work transferred to a system
E	Internal energy
n	Ratio, $\left(Internal\ Pressure/Cohesive\,energy\ density\right)$
S	Entropy

H	Enthalpy
G	Gibbs free energy
$\boldsymbol{d}$	Total solubility parameter
$\boldsymbol{d_l}$	Solubility parameter – nonpolar component
$\boldsymbol{d_t}$	Solubility parameter – polar component
$\boldsymbol{d}_d$	Solubility parameter – dispersion component
$\boldsymbol{d}_p$	Solubility parameter – polar component
$\boldsymbol{d}_h$	Solubility parameter – hydrogen bonding component
x	Mole fraction
$\boldsymbol{f}$	Volume fraction
R_o	Interaction radius
R_a	Distance (expressed as a radius) between two different HSP points
R_o^{liq}	Interaction radius based on polymer dissolution behavior in liquid solvents
R_o^{SCF}	Interaction radius based on polymer behavior in SCF
$\mathrm{n_D}$	Index of refraction
ε	Dielectric constant
$\boldsymbol{a}$	Thermal expansion coefficient
$\boldsymbol{b}$	Isothermal compressibility
$\mathrm{p_s}$	Saturation vapor pressure
B(T)	Tait parameters
$\mathrm{B_o}$	Material dependent parameter
$\mathrm{B_1}$	Material dependent parameter
$\mathrm{A_o}$	Material dependent parameter
$\mathrm{A_1}$	Material dependent parameter
$\mathrm{A_2}$	Material dependent parameter
γ	Surface tension
$\mathrm{P_S}$	Parachor parameter
k_D	Henry’s law constant